Lawrence Livermore National laboratory
University of California
Livermore, California 94551

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Historical Case Analysis of Chlorinated Volatile Organic Compound Plumes

Primary Authors

Walt W. McNab, Jr.
David W. Rice
Jacob Bear[1]
Richard Ragaini
Cary Tuckfield[2]
Curt Oldenburg[3]

Contributing Authors

Gregory Bartow[4]
Mike Brown[5]
Patrick Haas[6]
Christina Hubbard[7]
Janet Jacobsen[3]
Michael Kavanaugh[7]
Douglas Mackay[8]
William Mason[9]
Thomas McKone[10]
Michael Pound[11]
Heidi Temko[12]

March 8, 1999

1 Technion-Israel Institute of Technology
2 Savannah River Technology Center
3 Lawrence Berkeley National Laboratory
4 San Francisco Bay Regional Water Quality Control Board
5 U.S. Department of Energy
6 U.S. Air Force Center for Environmental Excellence
7 Private Consultant
8 University of Waterloo
9 Oregon Department of Environmental Quality
10 University of California, Berkeley
11 U.S. Naval Facilities Engineering Command
12 California State Water Resources Control Board

Environmental Protection Department

Environmental Restoration Division

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Preface

There are several national initiatives that continue to re-evaluate chlorinated volatile organic compound (CVOC) cleanup processes. These include efforts by the United States Environmental Protection Agency (US EPA) to reconsider the manner in which CVOC toxicity factors are developed; efforts by many investigators to evaluate the mechanisms and impacts of natural attenuation at individual sites; and efforts by the Department of Energy (DOE), the Department of Defense (DOD), and the US EPA to evaluate the use of enhanced natural attenuation during CVOC cleanup and to demonstrate new remediation technologies. Missing from these initiatives is a cross-cutting evaluation of the large amounts of CVOC historical case data that are available.

This document describes the findings and conclusions resulting from a study of nationwide historical case data gathered from sites with groundwater contaminated by CVOCs. The purpose of this initiative (the "Initiative") is to use a statistical perspective and data from multiple sites to evaluate the hydrogeologic, biogeochemical, and physiochemical factors affecting the extent and growth behavior of CVOC plumes in groundwater. This evaluation is important because of the significant role that plume behavior plays in the management of human health, environmental decision making, and resource risk evaluation.

The CVOC Initiative is a cooperative partnership between a variety of organizations and agencies involved in the cleanup of CVOC plumes. The Environmental Council of States, Interstate Technology and Regulatory Cooperation (ITRC) working group serves as a link to state regulatory bodies. The US EPA, DOE, US Navy, US Air Force, industry, and ITRC member states have provided CVOC historical case data in support of this Initiative.

The data management, statistical analysis, and modeling efforts conducted within the framework of the Initiative were performed by a team of scientists and environmental professionals from Lawrence Livermore National Laboratory (LLNL), Lawrence Berkeley National Laboratory (LBNL), and Savannah River Technology Center (SRTC). On behalf of DOE, LLNL has served as the overall Initiative Coordinator. Throughout the project, ITRC member states have been regarded as the appropriate entities to consider the development of any recommendations that would be warranted on the basis of the scientific evaluation of the historical case data, as presented here.

As part of this Initiative, two groups were formed: a Working Task Force (WTF) and a Peer Review Panel (PeerRP). The WTF focused on the technical issues of historical CVOC case data collection and analysis as well as preparing draft findings and conclusions based on the data analysis. The PeerRP was called upon to review key deliverables, raise technical issues, and review and comment on draft findings, conclusions, and recommendations. The members of the WTF are:

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- Doug Mackay, Ph.D., University of Waterloo,
- Bill Mason, Oregon Department of Environmental Quality,
- Curt Oldenburg, Ph.D., Earth Sciences Division, Lawrence Berkeley National Laboratory,
- Michael Pound, U.S. Navy, South West Division, Naval Facilities Engineering Command,
- Richard Ragaini, Ph.D., Lawrence Livermore National Laboratory,
- *David Rice, Lawrence Livermore National Laboratory,
- Heidi Temko, California State Water Resources Control Board,
- Cary Tuckfield, Ph.D., Savannah River Technology Center, Westinghouse Savannah River, Co.

* CVOC Historical Case Analysis Project Director

Executive Summary

Overview of the Study

Knowledge about the general patterns in behavior of chlorinated volatile organic compound (CVOC) plumes, their transformation daughter product plumes, and relationships between plume behavior and site variables is essential to managers and decision-makers engaged in CVOC plume investigation and remediation. By analyzing populations of plumes, likely CVOC plume behavior scenarios can be better understood.

The present study represents an attempt to understand the factors affecting the behavior of CVOC plumes in groundwater from a broad, statistically oriented perspective. One of the key issues in using historical case data is the often-unknown quality of the data, and yet these data are typically used as the basis for site cleanup decision making. Thus, a key goal of this study is to evaluate a large population of historical CVOC case data and evaluate which aspects of CVOC plume behavior and CVOC risk management can be supported by historical case data. It is reasonable to expect that by analyzing site-specific field data from a relatively large number of CVOC releases, the relationships between CVOC plumes and site characteristics can be identified, albeit on a statistical basis. As such, the general findings of this study are not necessarily applicable to any individual site. However, managers of specific sites will benefit from the analysis and its conclusions, as their understanding of plume behavior is enhanced through an examination of data from many sites. It is believed that focusing on the major factors influencing plume behavior will increase the efficiency of planning site investigation and cleanup operations.

Specifically, the following general questions involving the applicability of historical case data to CVOC risk management are addressed:

1. Can historical case data be used to predict CVOC plume behavior?
2. What are key uncertainties associated with evaluating CVOC plume behavior using historical case data and what other types of data are needed?
3. How may CVOC historical case analysis be used in CVOC cleanup decision-making?

A number of more specific questions of interest to researchers and managers of CVOC cleanup regarding the factors that are related to CVOC plume behavior are also addressed by this study. These questions include:

4. How often is a dense non-aqueous phase liquid (DNAPL) inferred to be present at sites within the CVOC historical data set and what is the relationship of inferred DNAPL presence to the plume length at a given site?
5. How often are transformation processes encountered in CVOC plumes in the data set and what are the relationships between the indications of transformations and plume length?
6. Do daughter product plumes behave differently compared to parent CVOC plumes?

7. What is the relationship of fuel hydrocarbon co-contamination to CVOC plume behavior?

Methodology

The primary analysis approach during this study was to identify and quantify trends and relationships in the data between plume characteristics (e.g., plume length) and site hydrogeologic, biogeochemical, and CVOC physiochemical variables using correlation analyses and population inference tests. To conduct the study, procedures for data collection and analysis included the following specific tasks:

1. Candidate sites were screened using a site checklist. Sites were accepted for inclusion in the study if: (a) data were available from at least six monitoring wells over a three-year monitoring period prior to remediation, (b) site plumes did not significantly daylight, (c) site plumes were not significantly affected by pumping in nearby wells, and (d) interpretation of plume length was not complicated by multiple CVOC sources. Once a site passed the screening and was accepted in the study, CVOC historical monitoring data were obtained electronically, and hydrogeologic data were extracted from site reports.
2. Mean values were estimated for site hydrogeological variables, such as groundwater velocity. Different variables required different approaches to quantify mean site values. For example, in the case of hydraulic conductivity, a representative mean site value was quantified by utilizing the geometric mean of values reported for individual monitoring wells through pumping tests or slug tests. Reductive dehalogenation potential was treated as a categorical variable, defined by the presence of certain reductive dehalogenation daughter products and supported by an analysis of trends in groundwater geochemistry.
3. The key plume characteristics, plume length and plume length growth rate, were estimated for all individual CVOCs at each site in the study. Plume lengths were estimated using an algorithm that used CVOC concentration data to systematically quantify the distance from the location of the reported maximum CVOC concentration in a plume to a distal 10-ppb, 100-ppb, or 1000-ppb contour. Relative plume growth rates were estimated on an individual CVOC basis using time-series analysis of plume data from individual sites.
4. Statistical analyses were performed to identify relationships between plume length and site hydrogeological variables, the physiochemical properties of individual CVOCs, and the identified biogeochemical transformation categories. Statistical tests included analysis of correlation, comparison of population means, and the development of a general linear statistical model.
5. Probabilistic plume modeling was employed to provide a mathematical conceptual framework to relate observed correlations to fate and transport mechanisms. The mathematical modeling provided an inferential line of reasoning that was used as a basis of comparison to the statistical reasoning used during the analyses of the CVOC field data. Agreements between the two approaches provided validation of the study findings.

The study involved the collection and analysis of data from 65 sites representing a variety of hydrogeologic settings and release scenarios (e.g., large industrial facilities, dry cleaners, and landfills). Data collection involved a variety of federal and state agencies and included participation from the U.S. Department of Defense, the Department of Energy, and private industry. Plumes were defined per CVOC per site, yielding a total of 247 plumes delineated by the 10-ppb contour and subsets of 134 plumes and 58 plumes delineated by the 100- and 1000-ppb contours, respectively. A total of 16 different CVOCs were included in the study.

Findings

An evaluation of the CVOC historical case data collected to date found the following general characteristics:

- The contaminant chemistry was generally found to be the most complete of the data types reviewed. Data on hydraulic conductivity and organic carbon content of soils and groundwater were less systematically collected and/or reported. Theoretically, these parameters should be key to understanding the fate and transport of subsurface contaminants.
- As an aggregate population, CVOC plume lengths are approximately lognormally distributed, although with some deviations. In particular, the frequency of small plume lengths appears to be under-represented in this data set based on a lognormal probability distribution model.
- Among the sites in this study, the longest CVOC plume lengths from each site are also lognormally distributed. Among these plumes, the median CVOC plume length was approximately 1600 ft, and 90% of the CVOC plumes in this study were less than approximately 6300 ft in length.
- There are no statistically significant differences between CVOC species with regard to their log-transformed 10-ppb plume lengths, including likely transformation daughter products such as *cis*-1,2-DCE and vinyl chloride.

Correlation analysis and population inference tests revealed a number of trends in the field data. These include:

- Plume lengths are positively correlated with maximum historical CVOC concentrations and mean groundwater velocity at each site.
- Based on the observed maximum historical concentrations, approximately 40% of the TCE plumes may be associated with DNAPL based on a 1% solubility limit rule-of-thumb, and approximately 10% of the TCE plumes may be associated with a DNAPL based on a 10% rule-of-thumb. Based on these solubility limit rules-of-thumb, the presence of DNAPL is suggested in a majority of cases where a 1000-ppb TCE plume can be defined.
- The effects of reductive dehalogenation on the plume length are measurable, but only when the influences of source area mass (maximum groundwater concentration) and groundwater velocity are factored out. Plume lengths adjusted for these variables are shorter when there is strong evidence of reductive dehalogenation. These results suggest

that the role of transformation processes in influencing CVOC plume lengths is relatively subtle. There is also evidence that plumes at sites exhibiting strong reductive dehalogenation show less plume growth than those from other sites.

- Large daughter product plumes do not commonly extend a large distance downgradient of the parent product plumes.
- The statistical association between fuel hydrocarbons, elevated bicarbonate alkalinity, and the presence of vinyl chloride plumes provides circumstantial evidence that fuel hydrocarbon co-contamination may be an important factor in the reductive dehalogenation of CVOC plumes in the historical case analysis data set. Elevated manganese concentrations at sites with vinyl chloride plumes is consistent with the presence of an anaerobic environment at these sites.
- Variability in maximum concentration between sites is positively correlated with literature derived CVOC-specific organic carbon partitioning coefficients. In addition, some positive correlation may exist between the Henry's Law constant and variability in maximum concentration between sites. Furthermore, there is a possible correlation between plume length and the Henry's constant once factors such as source strength and groundwater velocity are factored out. Although these relationships are statistically significant and are consistent with idealized conceptualizations of plume behavior, these results must be viewed as preliminary in nature. Further studies must be conducted to independently confirm these observations.

Monte Carlo simulation, using an analytical plume model and inferred probability distributions of hydrogeologic variables, was used to generate populations of synthetic plumes. Application of the same analytical approaches used for the field data to the synthetic plume data, yielded similar results in terms of plume length relationships.

Conclusions

This study provides the first statistical analysis of data from a relatively large population of CVOC plumes. From this analysis, the following conclusions result:

- This study demonstrates that broad trends in relationships between plume behavior and key site variables can be determined through the statistical analyses of historical field data from a large number of sites. This finding is important because it demonstrates that: (1) specific hydrogeologic conditions and contaminant release scenarios at individual sites are not so unique that expected overall trends in the data are completely obscured, and (2) useful average values for site variables such as hydraulic conductivity and groundwater velocity can be quantified in most situations.
- This study also shows that statistical methods, such as general linear models and comparison of probability distributions of plume length indices[1], are useful to quantify expected relationships between plume length and site and CVOC variables within a population of CVOC plumes. In addition, they provide population statistics that may be used to bound the uncertainty inherent in expected plume behaviors.

[1] Plume length index is defined as the plume length divided by the groundwater velocity and by the maximum groundwater concentration of the contaminant.

- This study provides quantitative confirmations that plume behaviors can be grouped and that these groupings are based on expected hydrogeologic processes.
- One of the major features of this study is that its analyses and conclusions are based primarily on actual field observations, i.e., data from actual CVOC plume historical cases. At present, there is no evidence that the historical case data can be used predictively outside the range of data reviewed. The strength of the conclusions arising from statistical analyses of the CVOC data are dependent upon data set characteristics, particularly the representativeness and the quality of the data. It must be noted that the plume length distributions, relative plume growth rates, and the types of CVOCs involved are reflective of the 65 sites in the project database exclusively. There is no way of ascertaining whether or not these distributions present an unbiased sample of the entire population of CVOC plumes across the U.S. without conducting a much larger survey on a vast scale. As more data are added to the CVOC historical data set, representativeness will be enhanced.
- Based on the rules-of-thumb as indicators of free-phase CVOCs, the results of this study suggest that the DNAPL may be influencing plume behavior to a certain extent, although, not in the case of daughter product species, e.g., *cis*-1,2-DCE, vinyl chloride, and possibly 1,1-DCA and 1,1-DCE in some cases. It must be emphasized that these inferences are based entirely on very general rules-of-thumb that have been established in the contaminant hydrology literature. In reality, there is no direct way of ascertaining whether or not DNAPLs are present at the sites given the data provided for this study. However, the relationships between plume length and reported maximum concentration are likely to reflect the overall strength of the source term, which may in turn be influenced by the presence or absence of DNAPL as well as the capacity for any residual DNAPL to be actively leached into groundwater.
- An important conclusion of this study is that the presence of a vinyl chloride plume indicates that reductive dehalogenation may be playing a role in reducing the extent of CVOC plumes at approximately one-third of the sites examined. In contrast, the presence of a *cis*-1,2-DCE plume in the absence of a vinyl chloride plume appears to indicate reductive dehalogenation rates that are insufficient to effectively reduce the extent of CVOC plumes at a site. Little evidence was found in the data to suggest that plume lengths and plume growth rates are substantially affected by reductive dehalogenation in these circumstances.
- Another important conclusion is that CVOC transformation rates through dehalogenation exert less impact on plume length than source strength and groundwater velocity. Thus, plumes with weaker source strength and slower groundwater velocities may be better candidates for the application of natural attenuation remedies.
- The statistical results of the CVOC historical case analysis suggest that the association between fuel hydrocarbons and reductive dehalogenation may be widespread. It is important to recognize, however, that the West Coast-bias in the site representation in the data set may influence these results. For example, sites from the eastern U.S., characterized by higher precipitation and therefore a greater preponderance of vegetation, may be characterized by larger quantities of natural organic carbon which would be

available to facilitate reductive dehalogenation. In such instances, the influence of fuel hydrocarbon co-contamination may be less pronounced.

Discussion and Recommendations for Future Work

It is clear that variability is a fundamental characteristic of CVOC sites and that conclusions stemming from the current study are general and should not be strictly applicable at any specific site. Although the emphasis in this study is on examining correlations between plume length and hydrogeologic variables, it is apparent that there is enormous variability in both plume length and maximum concentration.

Continued data collection is recommended because a more comprehensive data set would shed light on some of the questions not answered completely in this present study. These questions include:

- Are there significant differences in plume behavior across different geographic hydrogeologic regimes (e.g., as specified in Heath, 1984)?
- Is there a dependence of plume behavior on climatic factors such as mean annual rainfall, evapotranspiration rate, or vegetative cover at the site?
- What is the quantification of statistical relationships between site natural organic carbon content and (1) retardation of plume length or normalized plume length and (2) reductive dehalogenation? With regard to reductive dehalogenation in particular, a comparison of the roles of natural organic carbon and anthropogenic carbon sources (e.g., fuel hydrocarbons) would be of significant interest.
- Are there differences in the relationships of plume behavior to site variables, particularly the classes of plumes specifically excluded from this study, e.g., plumes that daylight. The use of exclusion criteria may systematically under-represent very short and very long plumes in the data set.

In summary, this study sets a precedent for future historical case analysis studies that might include:

1. A more detailed analysis of retardation phenomena contingent upon availability of soil organic carbon data.
2. Geostatistical analyses of plume spatial moments to include dispersion (in three dimensions) as a variable.
3. Development of a significantly expanded data set (i.e., hundreds of sites) which would allow subsets of site classes to be evaluated separately and then be compared to one another. The ultimate goal of such follow-on studies should be to develop a comprehensive statistical model for plume behavior.

This statistical model could provide:

1. Individual site investigators with a plume reference model against which a given plume may be compared and used to identify anomalous behavior.
2. Regulatory agencies with an integrated survey of plume behavior under a variety of conditions.

3. Validation for theoretical models and anecdotal studies of plume behavior within a probabilistic conceptual framework.

The results of this historical case analyses may be used by a site manager to develop initial site conceptual models and help focus characterization resources on data that will be most useful in confirming or denying conceptual model hypotheses. In addition, the study provides information on the types of data that are not currently being collected that should be collected in the future, e.g., organic carbon analysis.

1. Introduction

1.1. Background

Knowledge about the general patterns in behavior of chlorinated volatile organic compound (CVOC) plumes, their transformation daughter product plumes, and relationships between plume behavior and site variables is essential to managers and decision-makers engaged in CVOC plume investigations and remediation. By analyzing populations of plumes, likely CVOC plume behavior scenarios can be better understood.

To date, CVOC groundwater plume behavior has been studied at a large number of individual sites, but has never been evaluated through a systematic statistical analysis of available data on a relatively large number of existing plumes. Individual site studies indicate that each site features its own individual characteristics (e.g., geological structure, aquifer parameters, transport, and chemical and biological transformation mechanisms) which, in turn, produce a plume that has its own particular morphological features (e.g., length, depth, and rate of growth). Unfortunately, because field data are often sparse as a result of economic and sampling constraints, a thorough, detailed understanding of plume behavior at a given site is more the exception than the rule. Nevertheless, the same flow, transport, and transformation mechanisms influence essentially all CVOC plumes, although at a magnitude that may vary greatly from site to site. Thus, it is reasonable to expect that by analyzing site-specific field data from a relatively large number of CVOC releases, the relationships between CVOC plumes and site characteristics can be identified on a statistical basis. The key is to gather and analyze data from a large number of plumes.

Several previous studies have attempted to compare CVOC plume behavior using a limited number of sites, focusing primarily on the effectiveness of the groundwater pump-and-treat techniques. Doty and Travis (1991) evaluated 16 sites, US EPA evaluated 19 sites (Keely, 1989; US EPA, 1989) and 24 sites (US EPA, 1992), the National Research Council (1994) evaluated 72 sites, and Bartow and Davenport (1995) evaluated 37 sites. None of these previous studies has attempted to evaluate CVOC plume extent and growth behavior, which are primary goals of this study, nor did most of these previous studies use a statistically meaningful data set.

1.2. Project Objectives

The present study represents an attempt to understand the factors affecting the behavior of CVOC plumes in groundwater from a broad, statistically oriented perspective. One of the key issues in using historical case data is the often-unknown quality of the data, and yet these data are typically used as the basis for site cleanup decision making. Thus, a key goal of this study is to evaluate a large population of historical CVOC case data and evaluate which aspects of CVOC plume behavior and CVOC risk management can be supported by historical case data. Further, knowing which key variables are significantly related to aggregate plume behavior, and which are less important, allows knowledgeable decisions to be made to the allocation of resources to site characterization and to remedial activities.

Because the results of any such evaluation are necessarily presented in a probabilistic format, they will mainly serve those persons interested in broad trends in CVOC plume behavior across many sites. As such, the general findings of this study are not necessarily applicable to any individual site. However, managers of specific sites will benefit from the analysis and its conclusions, as their understanding of plume behavior and the major factors that are related to plume behavior will have been enhanced through an examination of data from many sites. It is believed that focusing on these major factors will increase the efficiency of planning site investigation and cleanup operations.

Specifically, the following general questions involving the applicability of historical case data to CVOC risk management are addressed:

- Can historical case data be used to predict CVOC plume behavior?
- What are key uncertainties associated with evaluating CVOC plume behavior using historical case data and what other types of data are needed?
- How may CVOC historical case analysis be used in CVOC cleanup decision-making?

A number of more specific questions of interest to researchers and managers of CVOC cleanup regarding the factors that are related to CVOC plume behavior are also addressed by this study. These questions include:

- How often is a dense non-aqueous phase liquid (DNAPL) inferred to be present at sites within the CVOC historical data set and what is the relationship of inferred DNAPL presence to the plume length at a given site?
- How often is there evidence of transformation processes in association with the CVOC plumes in the data set and what are the relationships between the indications of transformations and plume length?
- Do daughter product plumes behave differently from parent CVOC plumes?
- What is the relationship of fuel hydrocarbon co-contamination to CVOC plume behavior?

2. Methods

2.1. Overview of Project Data Analysis Approach

In principle, the behavior of a contaminant plume in an aquifer is affected by a number of variables. These include the geologic features of the aquifer, the hydraulic properties of the porous medium (including its spatial variability), the chemical composition of the indigenous water, the chemical nature of the contaminant of interest and its interactions with other aqueous constituents, the geologic substrate, the local microbiota, etc. See Appendix A, Sections A-1 and A-2 for additional details. To understand the factors affecting the behavior of CVOC plumes in groundwater from a broad, statistically oriented perspective, the basic process of the CVOC historical case analyses was to first define plume characteristics such as plume length. The next step was to assess the degree of correlation of these plume characteristics with mechanisms and processes of CVOC transport and transformation as manifested by hydrogeologic, biogeochemical, and physiochemical variables.

To provide guidance in the pursuit of the project objectives, a set of general hypotheses were developed prior to the collection and analysis of the data. These hypotheses were established to provide focus and scope to the project and to aid in developing the appropriate testing methodologies. Other hypotheses were developed and tested during the course of the data analysis. The initial hypotheses include:

- Relationships between plume characteristics and site and CVOC physiochemical variables that would be expected to influence plume behavior (e.g., site hydraulic conductivity, biotransformation rate, volatilization potential) should not be completely masked by variability in site-specific features. Examples of such features include the presence of preferential subsurface flow pathways or conduits, multiple hydrostratigraphic units, or a complex release history. Rather, the variability in the site-specific features will simply contribute random noise in the statistical relationships being examined.
- CVOC plumes characterized by evidence of transformation processes will exhibit different plume behavior compared to CVOC plumes without this evidence. In particular, plumes undergoing reductive dehalogenation, as well as those composed of 1,1,1-TCA (a compound which transforms abiotically in groundwater environments), would be expected to be relatively shorter in length. An important assumption of this hypothesis is that plumes undergoing reductive dehalogenation can be distinguished in a systematic way from those that are not.
- Among the physical and biogeochemical variables that could be quantified for sites and CVOCs in the study, groundwater velocity and indications of transformation processes should be expected to be significantly related to plume characteristics. Other variables (e.g., age of the plume, depth to groundwater, retardation coefficient) would be weakly related to plume characteristics by comparison. This hypothesis is based upon previous experiences and best professional judgment of the investigators.

Once the CVOC historical data base was established (See Section 3.2, below), analysis proceeded according to four general steps:

1. Mean values were estimated for the site hydrogeological variables: hydraulic conductivity, groundwater velocity, and geochemical indicator parameters. Different variables required different approaches in deriving site specific means. For example, a representative site mean hydraulic conductivity was derived from the geometric mean of hydraulic conductivity values reported for individual monitoring wells through pumping tests or slug tests. Mean hydraulic gradient was derived based on mean values reported in consultant reports or was estimated from potentiometric surface maps.
2. Reductive dehalogenation activity was categorized according to the presence of certain CVOC reductive dehalogenation daughter products, supported by an assessment of the groundwater geochemical indicators (see discussion in Appendix A, Section A-2, Transformation of CVOCs). Concentrations of geochemical indicators of transformation, such as chloride ion concentrations, were estimated using the 90^{th} percentile concentration from each site and geochemical indicator compounds. In evaluating the data, hydrogeological variables provided in consultant reports were taken at face value.

3. The primary plume characteristics used in this study are plume length and plume length growth rate. These characteristics were estimated for each CVOC at each site in the study. Plume length was defined by the distance from the location of the maximum CVOC concentration in the plume (the presumed source area) to the most distal 10 part-per-billion (ppb), 100-ppb, or 1000-ppb isoconcentration contour location. This estimation was made using an algorithm that systematically quantified plume length based on analysis of site-specific spatial distributions of CVOC concentration data. A description and discussion of the plume length algorithm is presented in Appendix B. Individual CVOC plume growth rates were estimated using time series analysis of plume data from a given site.

4. Statistical analyses were performed to identify relationships between plume length and site hydrogeological variables, reductive dehalogenation activity, and physiochemical properties of individual CVOCs. Statistical tests included analysis of correlation, comparison of population means, and the development of a general linear model (GLM). The GLM was used to quantify the contributions of site variables to the observed variance in plume characteristics. This provided a means for comparing individual plume characteristics to other plumes from similar hydrogeologic settings and to facilitate the identification of anomalous plume behavior or morphology. Details of the application of the GLM to the CVOC historical case data set are presented in Appendix C.

Any study using statistical analyses of field data would be expected to yield findings that are entirely empirical in nature. Therefore, it is important to view the results of the CVOC historical case data analysis within the framework of a mathematical conceptual model of plume behavior. In principle, predictions of plume behavior could be prepared using theoretical models that describe plume evolution on the basis of the fundamental laws governing flow and transport in porous media. Such models include the consideration of factors (e.g., hydraulic conductivity, hydraulic gradient, transformation and adsorption coefficients) that determine the behavior of a contaminant plume at a specific site. Once these factors and associated variability are known for a given site, the plume's behavior at that site can be predicted theoretically. Unfortunately, under field conditions, we are confronted with two fundamental difficulties:

1. At most sites, there is no practical way to obtain information on all the relevant site-specific factors influencing the plume. This is especially true with regard to chemical and biological transformations that may have a pronounced effect on the CVOC plumes.

2. Uncertainty exists with respect to practically all factors and associated variability that affect plume characteristics at any particular site, due to the heterogeneity of the domain, lack of information on boundary conditions, etc.

To address these difficulties, probabilistic plume modeling was employed during the application of the mathematical conceptual model, parallel to the analyses of field data. This probabilistic plume modeling involved the use of a Monte Carlo simulation technique to generate a large number of synthetic plumes for cases for which analytical solutions to the transport equation are available. Probability distributions of the site hydrogeologic variables were obtained whenever possible from the site data collected in the study. Essentially, this modeling effort produced a parallel, synthetic data set to compare to the field data.

2.2. Definitions and Assumptions

During the analysis of the CVOC historical case data, a *variable* was defined as a measurable quantity that describes some feature of the plume itself or its local hydrogeological environment. The former is referred to as a “dependent”, or “plume characteristic variable”, while the latter is referred to as an “independent site variable”. The magnitude of a plume characteristic variable presumably is related to, or dependent upon, the magnitude of one or more independent site variables where the average of each variable changes from site to site. Variables can be grouped as:

<u>Plume characteristic variables</u> (i.e., dependent variables). These include plume length and plume growth rate. Here, *plume length* is defined, per CVOC, as the distance from the well where the maximum historical concentration was measured to the most distal location of the concentration contour of interest. Where possible, plume lengths were developed for three isoconcentration contours: 10 ppb, 100 ppb, and 1000 ppb. These isoconcentration contours were chosen because they addressed the detection limits typically reported as well as the ranges of concentrations encountered at the majority of sites. The CVOC concentration data can be quite variable at low concentrations, and projected CVOC plume boundary estimations at concentrations less than 10 ppb can be strongly influenced by this variability. Thus, plume lengths defined by concentrations less than 10 ppb were not quantified.

In the context of this study, plume length and plume growth rate, i.e., change in plume length as a function of time, are highly idealized concepts of plume behavior given the complex morphology expected of subsurface groundwater plumes. Nevertheless, given the limited spatial resolution provided by the monitoring well networks at most of the sites in the study, and given the number of sites involved, such a simplified model is appropriate in the context of this study.

In addition, while it is recognized that detailed delineation of CVOC plumes often involves the vertical dimension, it is assumed in this study that concentrations may be averaged across the vertical extent of the aquifer(s), so that plumes are effectively treated as two-dimensional bodies. This assumption, which must be placed in context of the overall goals of the study, is based on the common observation that the horizontal extent of most plumes usually exceeds the vertical extent by a large factor.

In this study, three different types of independent variables were evaluated for their possible relationship to plume characteristics, principally plume length:

<u>Hydrogeologic variables</u> (i.e., independent site variables). These include (among others): source strength and groundwater velocity.

- *Source strength*. The magnitude of the reported maximum concentration within a CVOC plume was assumed to reflect the strength of the plume’s source. In the case of parent CVOCs, this may involve DNAPL dissolution, whereas for daughter product plumes the maximum concentration may be indicative of the area where the majority of the mass transformation is taking place. The spatial location of the reported maximum concentration was used to estimate the best approximation of the location of the CVOC source.
- *Groundwater velocity*. Mean groundwater velocity was calculated using Darcy’s Law for each site that provided hydraulic conductivity and gradient data. The correlation of the

maximum CVOC plume length per site was then compared with the corresponding mean groundwater velocity, or range of velocities, by correlation analysis.

Biogeochemical variable (i.e., independent site variable). This refers specifically to the indications of reductive dehalogenation at a given site and is treated categorically rather than in a continuous manner. Most variables are assumed to be *continuous*; their values are reported as real numbers on a continuous scale of measurement. The average for each of the independent site variables is calculated and used as a representative measure for each site in the data analyses. Ideally, mean CVOC biotransformation rates would be quantified as a continuous variable at sites where reductive dehalogenation is occurring. Statistical analyses of potential relationships between the mean biotransformation rate and plume length could then be conducted. However, given the limited spatial and temporal data available from many of the sites in the study, the systematic quantification of biotransformation rates at most of the sites was considered unfeasible. Therefore, reductive dehalogenation was treated as a *categorical* variable. A categorical variable is then represented by an integer value for each specific category.

Assignment of one of three reductive dehalogenation categories was made to all CVOC plumes at a given site. The three categories were: strong, weak, or no reductive dehalogenation potential. The categorical assignments were based upon the presence of the likely daughter products of the chloroethene reductive dehalogenation sequence, *cis*-1,2-DCE and vinyl chloride. Groundwater geochemical data from the sites were used to check the validity of the category assignments (see Appendix A, Section A-2.1.1, Site Categorization). Populations of plume lengths of CVOCs from different categories of sites were then compared to assess the effects of transformations on plume length.

CVOC physiochemical variables. These include specific properties of individual CVOCs, such as the organic carbon partitioning coefficient, Henry's Law constant, solubility, and vapor pressure that may indicate a relationship to plume behavior or CVOC concentrations. The plume lengths and maximum concentrations of individual CVOC species were compared to specific CVOC organic carbon partitioning coefficient, Henry's Law constant, solubility, and vapor pressures using correlation analysis.

2.3. Historical CVOC Case Data Collection

2.3.1. Site Selection Process

The purpose of the data collection and management process was to collect enough plume data in sufficient detail to test hypotheses regarding plume behavior. This included collecting information on a broad spectrum of site-specific variables that may influence plume behavior. To focus on the hypotheses of the study, the scope covered by this research excluded the following scenarios when they could be readily identified:

- Plumes that daylight substantially into surface water.
- Plumes dominated by any pumping and treating operation.
- Plumes where interpretation of plume length was complicated by multiple sources.
- Plumes with grossly indeterminate shape.

All other plumes were assumed to comprise a sufficient set from which the typical and general behaviors of CVOC plumes could be identified, while minimizing the influence of less common and more complex circumstances. Many CVOC plumes have had primary source removal either by actual physical removal of a leaking container or excavation of a disposal area or by hydraulic control of the secondary source area, without necessarily exercising hydraulic control on the distal portion of the plume. These sites were not excluded from the study.

The plume data gathering progressed in several steps (Fig. 2-1). First, partner organizations in the CVOC Initiative attempted to identify available plumes for analysis by completing a Plume Screening Checklist for candidate sites. This checklist was intended to identify which sites had a sufficient data set available for a plume to be considered by the Data Collection Team for inclusion in the historical case analysis. The CVOC Plume Screening Checklist is presented in Appendix D. Typically, the participant organization could find the information needed to complete the Plume Screening Checklist in the site Record of Decision (ROD), Remedial Investigation (RI), annual monitoring, or other similar reports.

Next, a plume screening process that identified plumes with a minimum data requirement was implemented. Plumes that passed this minimum criterion became candidates for further selection by the Data Collection Team. The key CVOC plume screening criterion was the availability of data from at least six monitoring wells sampled over at least three sampling intervals conducted over at least two years prior to the initiation of hydraulic control activities. Thus, no further screening evaluation was needed for a given plume if a participant organization case worker could not answer “yes” to this criterion. The Data Collection Team then decided which nominated sites were to be put into the Statistical Analysis of VOCs in the Environment (SAVE) database. See Figure 2-2 for the basic SAVE database structure and Appendix E for further details.

For legal and practical reasons, site names were not used in any reports issued pursuant to this study. Instead, generic site sequence numbers were assigned to each site for identification purposes. However, the site names are included in the database maintained by LLNL. Access to this database is allowed only with permission of LLNL.

Since the purpose of this study is to evaluate relationships between plume characteristics and site variables, identifying such relationships does not necessarily depend on having an ideally representative sample population so long as the sample population exhibits a broad range of plume characteristics and site variables. Such variability is well represented in the database; site historical and hydrogeological conditions for each CVOC plume analyzed are presented in Appendix F. Potential biases that may be in a data set gathered in this manner will be considered in the discussion of the study results.

2.3.2. Data Collection Process

LLNL Staff or CVOC Data Collection Team representatives called and discussed the data needs with the site responsible party and their consultant and ascertained what information could be obtained in electronic format or copied from reports. Once the electronic data were received, the CVOC Data Collection Team contacted state case managers and if possible, site consultants, to discuss site characteristics and specific data gaps, and to obtain data not available electronically. Documents were then either copied by the data contributor or borrowed for copying at LLNL. Electronic data were reformatted before being finalized in the SAVE database. Data entered into the SAVE database were queried and used as a basis to conduct the statistical analyses.

2.3.3. Distribution of CVOC Site Data

An initial data collection goal of the study was to include data from up to 400 sites nationwide. For several reasons, this goal proved to be unattainable within the time frame allotted for the present data collection efforts. These reasons include:

1. Many sites did not meet our screening criteria.
2. Electronic data were not available or not accessible.
3. Legal concerns by the responsible party.
4. A lack of good quality data.
5. Uncooperative responsible parties were.
6. Difficulty in making contact with the individual who had authority to release and provide historical case data.

While over 188 screening checklists were received, only 110 were accepted as representing usable sites. Among these, a site with a usable checklist was sometimes dropped because not all of the data needed to adequately define the plume were received. While the military and governmental sites added to the geographic diversity of the data set, requests for data from state agencies and environmental consulting firms proved to be most productive in the western states of California and Oregon.

A total of 65 sites were selected as the core data set for the analyses of this study. These represent a distillation of the 188 sites that expressed an interest in participating in the study as indicated in the screening checklists. Sites beyond the original 65 sites that had subsequently supplied data for the project were used for validation analyses.

CVOC plume lengths were identified for each CVOC at each site based on the plume length algorithm discussed in Appendix B. Among the 65 sites, 247 individual CVOC plumes, including parent CVOC and daughter product plumes, as defined by a plume length practical limit estimation of 10 ppb, were identified. In addition, subsets of 134 plumes defined by the 100-ppb contour and 58 plumes defined by the 1000-ppb contour were also identified. Fewer 100-ppb and 1000-ppb plumes were delineated because the low CVOC concentrations at many of the sites.

Fig. 2-1 SAVE Database Structure : Statistical Analysis of VOCs in the Environment

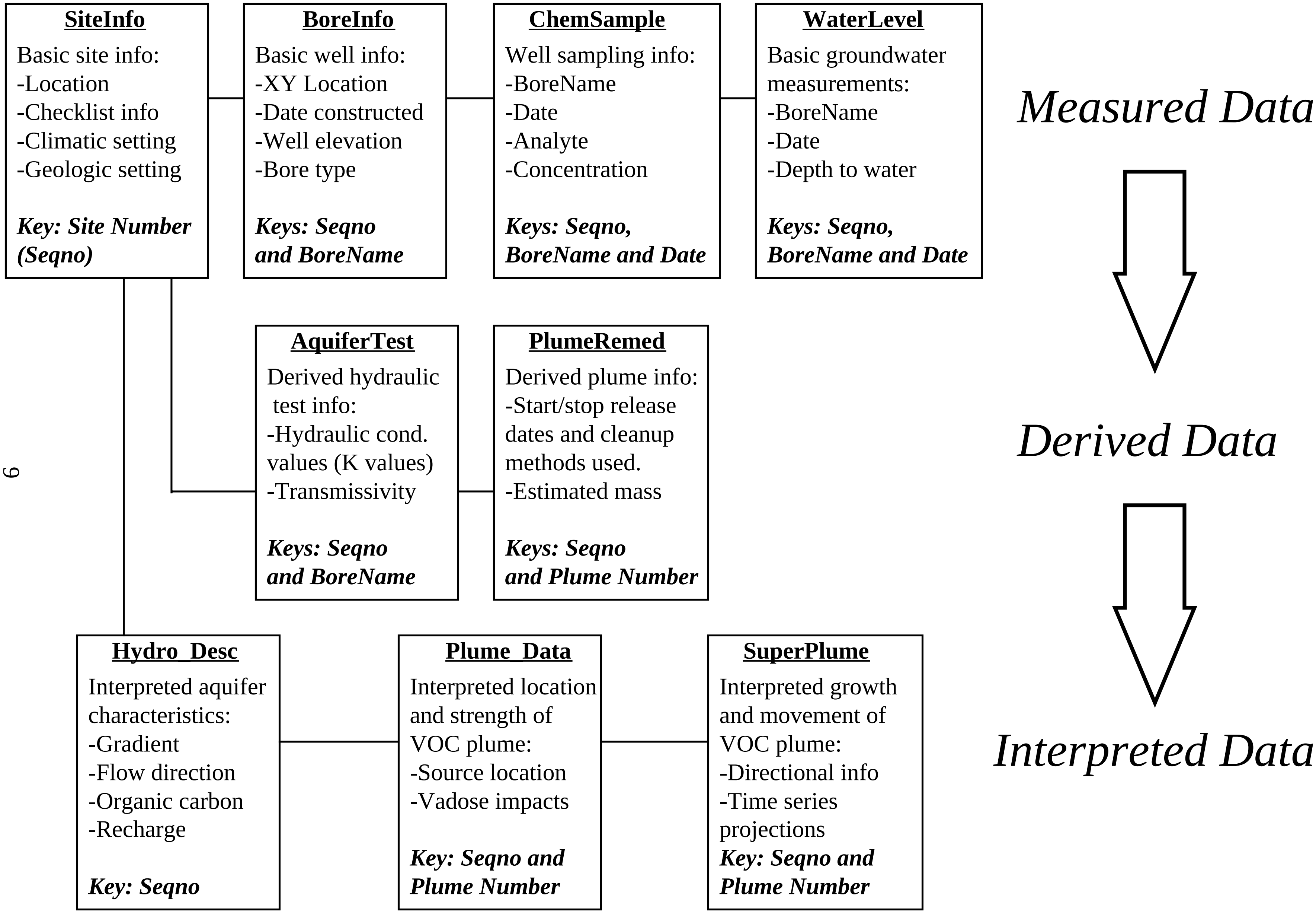
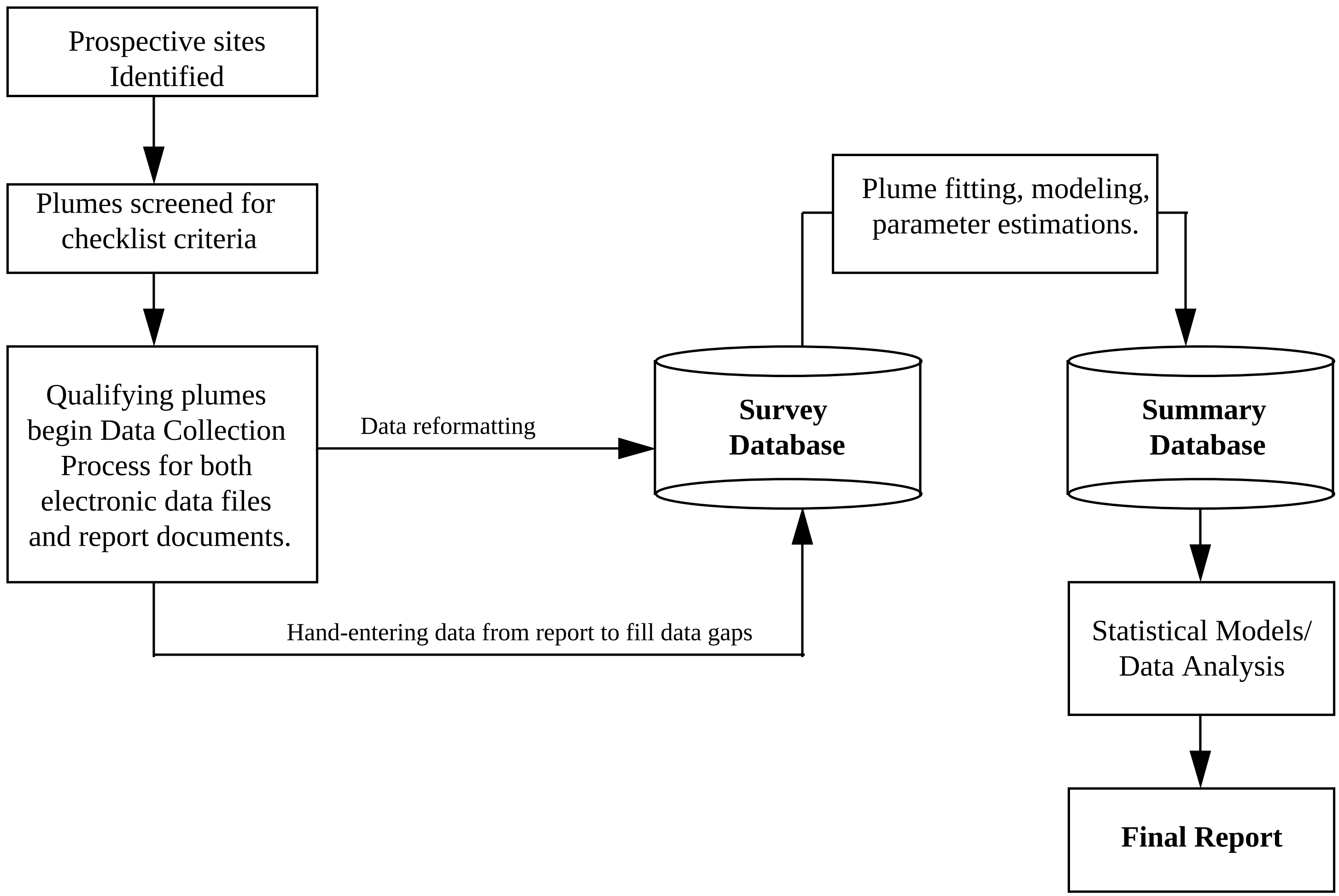


Fig. 2-2 Data collection process for adding data to the SAVE Database.



3. Overview of Findings

3.1. General Characteristics of the CVOC Historical Case Data Set

Among all of the CVOC plumes included in this study that were defined by the 10-ppb contour, 90% of the plume lengths evaluated do not currently extend beyond approximately 6300 ft downgradient of the area of maximum CVOC concentration. This is not to imply that all CVOC plumes will be shorter than 6300 ft. Ten percent of the plumes in the CVOC historical data set were longer and some were much longer.

The number of 10-ppb plumes distributed among the 16 different types of CVOCs that were encountered in the database is shown in Table 3-1. TCE constitutes the largest population of 10-ppb plumes (55 plumes). This is followed by PCE (32 plumes), with four other CVOCs (1,1-DCE, *cis*-1,2-DCE, 1,1,1-TCA, and vinyl chloride) each yielding at least 20 plumes, and 1,1-DCA providing 18 plumes. The remaining 41 plumes are distributed among a variety of other chlorinated hydrocarbons.

The sites included in the database, to date are, distributed across the country with the largest number of sites (40) located in states in the West Coast States (Fig. 3-1). Even though the distribution of sites is heavily weighted toward the West Coast, an enormous variability among CVOC historical case data set plumes exists. For example, the relationship between plume length and reported maximum concentration for 55 TCE plumes is shown on Figure 3-2, with several non-TCE plumes included to represent all 65 sites. From Figure 3-2, it is apparent that plume lengths and reported maximum concentrations from West Coast sites are evenly scattered within the entire distribution of plume lengths and reported maximum concentrations observed in the data set.

The degree of characterization of the CVOC sites in the data set is difficult to assess, but the number of monitoring wells may be used as a crude measure of the level of site characterization. The distribution of the number of monitoring wells per site with respect to four broad types of sites used for data, namely (1) Department of Defense (DOD), (2) Department of Energy (DOE), (3) industrial (including dry cleaning, grain storage, semiconductor manufacturing, and others), and (4) landfill, is shown on Figure 3-3. In the present data set, there are 15 DOD sites, 18 DOE sites, 28 industrial sites, and four landfills. The industrial sites are generally characterized by fewer wells than the DOD or DOE sites. Ninety percent of the industrial sites have 40 or fewer monitoring wells, compared to 50% of the DOD sites and 40% of the DOE sites. The number of monitoring wells at the DOD and DOE sites is more evenly distributed over the categories shown on Figure 3-3. The only sites with 100 or more monitoring wells are either DOD or DOE sites.

The number of monitoring wells per site does not correlate well with either plume length or maximum historical TCE concentration (Fig. 3-4). Of the 25 TCE plumes longer than 1000 ft shown on Figure 3-4, four were characterized by fewer than ten wells, and 10 others by between 11 and 50 wells. The relatively small number of wells used to characterize long plumes in some cases raises the question of how well those plumes have been characterized. Also worth noting is that the three longest TCE plumes span three orders of magnitude in maximum concentration, and the three shortest plumes, two orders of magnitude. Conversely, over each order of magnitude in the maximum historical TCE concentrations shown, the spread in plume length is two orders of magnitude or less.

The range of plume length and reported maximum concentration for the TCE plumes is shown by site type in Figure 3-5. Plumes from DOD, DOE, and industrial sites span over four orders of magnitude in terms of the reported maximum concentration of TCE. The range of plume length is slightly larger for DOD (over two orders of magnitude) and DOE (over one order of magnitude) sites compared to industrial sites. DOD and DOE sites have both the longest and the shortest plume lengths of all TCE sites in the data set.

3.2. Summary of CVOC Plume Characteristics

The longest (maximum) CVOC plume length at each site, irrespective of the type of CVOC measured, may be used to develop conservative site plume length frequency distributions. The distributions, which are approximately lognormal in nature, are shown on Table 3-2 for the 10-, 100-, and 1000-ppb-defined plumes. In general, 10-ppb plumes are typically on the order of 20% longer than 100-ppb plumes at most sites, whereas the 100-ppb plumes are on the order of 50% longer than the 1000-ppb plumes where the three coexist. Among the individual CVOCs represented in the data set, two observations emerge from summary statistical analyses:

1. Plume lengths defined by the 10-ppb isocontour are approximately lognormally distributed, although with some deviations. For example, an inference test of normality (Shapiro-Wilk *W*-Test) on the log-transformed plume length data indicates a statistically significant departure from an assumption of normality in the log distributions of plume lengths. In particular, short plume lengths appear to be under-represented and shorter than expected in this data set based on a log-normal probability distribution model. These findings are explored further in Appendix C.

2. There are no statistically significant differences in log-transformed 10-ppb plume length populations between the various CVOCs represented, based on an analysis of variance, or ANOVA (refer to Appendix C). This finding is important for a number of reasons. Use of the entire plume data set for certain correlation analyses would require that there are no significant differences between plume length populations among different CVOCs. From a process-oriented perspective, the lack of statistically significant differences in plume lengths between CVOCs holds important implications for the relationship between parent contaminants and transformation daughter product species. For example, a statistical equivalence in plume lengths between parent and daughter CVOCs may imply that the daughter product plumes are affected by attenuation processes (e.g., subsequent transformations, dispersion, volatilization). If daughter products are not attenuated in some manner, then the accumulation of daughter product mass would eventually yield significantly longer daughter product plumes. Alternatively, this finding may suggest that variability in physical transport variables such as the rate of advection may influence plume behavior more strongly than biogeochemical variables.

For 141 of the 247 plumes defined by the 10-ppb contour, a sufficient monitoring history existed to permit estimation of plume growth rates for comparative purposes. This corresponds to at least one CVOC plume from 48 of the 65 sites studied. Rank correlation analysis, with the rank of the annually averaged plume length as the dependent variable and the rank of the monitoring year as the independent variable, was used to quantify the proportion of plumes undergoing growth, shrinkage, or exhibiting no significant trend (See Appendix A, Section A-2.1.4). The median time period used for evaluating plume growth was six years, with a range between three and 15 years. Among plumes from sites exhibiting strong evidence of reductive dehalogenation, roughly equal numbers of plumes appeared to undergoing either a significant increase or decrease in length with time. In contrast, among plumes from sites lacking strong evidence of reductive dehalogenation, approximately twice as many plumes appeared to be increasing in length as opposed to exhibiting a decline.

3.3. Correlation of Plume Behavior with Hydrogeologic and Chemical Variables: A Summary

Analyses of the data collected in this study have shown statistically significant trends involving certain aspects of CVOC plume behavior and all of the independent variables discussed in Section 2.2, e.g., source strength, groundwater velocity, and biotic and abiotic transformations. The relationships between plume length and the variables related to the physics of contaminant transport, namely the roles of the source term and groundwater velocity, are the strongest. For example, a statistically significant correlation is observed between plume length and maximum concentration, with the correlation improving when higher concentration contours were used to define plume length (i.e., 100-ppb and 1000-ppb defined plumes). This finding may reflect the increasing proximity to the source area, where variability in maximum concentration would be expected to have a stronger relationship to the variability in plume length.

Reported maximum concentrations for individual CVOCs have been used by some workers as evidence for the presence of an active DNAPL source based on certain established rules-of-thumb, such as 1% or 10% of the solubility limit (Newell and Ross, 1991; and Feenstra and Cherry, 1988, respectively). Table 3-3 summarizes the fraction of plumes where reported maximum concentrations greater than the 1% and 10% solubility limits were observed for CVOCs represented by more than 10 plumes in the data set. Approximately 40% of the TCE plumes may be associated with DNAPL based on a 1% solubility limit rule-of-thumb and approximately 10% of the TCE plumes may be associated with a DNAPL based on a 10% rule-of-thumb.

The results of this study suggest that, in general, a high maximum CVOC concentration at a given site is often associated with a relatively long plume. This is especially true when plume length is defined with reference to higher concentration contour thresholds (e.g., 100- or 1000-ppb plumes). When these higher concentrations are used to define plume lengths, the proportion of plumes that are potentially associated with DNAPL increases. In particular, based on 1% and 10% solubility limit rules-of-thumb, maximum concentrations suggest the presence of DNAPL in a majority of cases where a 1000-ppb TCE plume may be defined. See Appendix A.

Plume length also correlates with the groundwater velocities estimated for sites in the data set (See Appendix A). In general, CVOC plume lengths appear to be much better correlated with different CVOCs at the same site than with the same CVOC across multiple sites. For example, the median ratio of the longest plume length to the shortest plume length among CVOCs at individual sites is approximately 3.3; whereas the median ratio of longest plume length to shortest plume length for individual CVOCs across multiple sites (for CVOC species represented by at least 6 plumes) is approximately 140. This analysis, aside from the other statistical tests, also suggests that site physical conditions are much more important in determining plume length than biogeochemical and physiochemical properties of the individual compounds.

In contrast to readily apparent relationships observed with the physical contaminant transport variables, clear relationships between CVOC transformation process categories or physiochemical variables and plume length are not apparent upon first inspection. For example, a plume's reductive dehalogenation category appears to have little relationship to plume length variability in comparison to other factors such as source strength or groundwater velocity. However, when the effects of these site variables are factored out using an indexing scheme or multivariate statistical analysis, a significant relationship between reductive dehalogenation categories and plume length becomes apparent.

Based on the presence or absence of *cis*-1,2-DCE and vinyl chloride reductive dehalogenation daughter products, the CVOC sites sampled in this study are divided roughly into equal thirds in terms of no evidence of reductive dehalogenation (no *cis*-1,2-DCE or vinyl chloride plumes), weak evidence of reductive dehalogenation (*cis*-1,2-DCE plumes but no vinyl chloride plumes), and strong evidence of reductive dehalogenation (vinyl chloride plumes present) (See Appendix A, Section A-2.1.1). Analyses of plume lengths from these three groups suggests that CVOC plumes are significantly shorter at sites where a vinyl chloride plume exists compared to plumes from other sites, after the effects of other variables such as source strength and groundwater velocity are factored out.

There is also some evidence to indicate that CVOC plumes at sites characterized by vinyl chloride plumes may exhibit lower growth rates. In contrast, the presence of a *cis*-1,2-DCE plume in the absence of a vinyl chloride plume indicates reductive dehalogenation rates that are insufficient to effectively reduce the extent of CVOC plumes; little evidence exists to suggest that plume lengths and plume growth rates are substantially affected by reductive dehalogenation in these circumstances. This finding is consistent with a survey of geochemical indicator species at these sites. In contrast to sites with vinyl chloride plumes, sites with only *cis*-1,2-DCE plumes present much less convincing evidence that fuel hydrocarbon oxidation is driving the biogeochemical setting toward a significant reductive dehalogenation environment.

A statistical evaluation of spatial relationships between daughter product and parent product plumes is not a straightforward process. During this study, plume lengths were defined for each CVOC with respect to the location of maximum historical concentration of that particular CVOC. This process of defining plumes was applied consistently to all CVOCs at all sites within the study because the precise source area or source area(s) were often unknown or unspecified. Given the spatial and temporal variability associated with CVOC plumes, and the sensitivity of inferred plume morphology to monitoring well locations, we concluded that measuring daughter product plume lengths with respect to the location of maximum concentration of the suspected parent product could not be justified *a priori*. Therefore, indirect methods of analysis were required in the context of this study to assess spatial relationships between daughter and parent product plumes (See Appendix A, Section A-2.1.3 and Appendix B for an expanded presentation of these methods and findings).

With regard to the spatial relationships between parent and daughter product CVOC plumes, it appears that, in general, daughter plumes do not typically extend much farther downgradient than the parent product plumes. In summary, evidence to support this conclusion includes:

1. There appears to be a lack of significant differences in plume length distributions between parent and daughter compounds (e.g., vinyl chloride plume lengths are not systematically longer than TCE plume lengths) (Appendix C, Fig. C-1).
2. Parent product compounds (e.g., PCE, TCE) form longer plumes than the probable daughter product compounds (e.g., *cis*-1,2-DCE, vinyl chloride) in the majority (73%) of the cases observed (Table 3-4).
3. The separation between parent and daughter product maximum concentration locations within co-mingled plumes is usually not large compared to the maximum plume length at the given site. Plume lengths are measured with reference to the location at which the reported maximum concentration was measured (i.e., the presumed source area). Among likely parent-daughter compound combinations (e.g., TCE and *cis*-1,2-DCE, *cis*-1,2-DCE and vinyl chloride), the distances between the respective maximum concentration locations are on the order of 10% to 25% of the maximum plume length at most sites.

Among the CVOC physiochemical and source strength variables, significant correlations appear to exist between the variability in maximum concentration between sites and both the organic carbon partitioning coefficient and the Henry's constant. In addition, there is a possible correlation between plume length and the Henry's constant, once factors such as source strength and groundwater velocity are accounted for through the plume length index. Although these relationships are statistically significant and are consistent with idealized conceptualizations of plume behavior, these results must be viewed as preliminary in nature; further studies should be conducted to independently confirm these observations.

All of these findings are discussed in detail in Appendix A.

Table 3-1. Summary of the number of different types of CVOC plumes that were recognized in the historical case data set using a range of isoconcentration contours.

CVOC	10-ppb plumes (from 65 sites)	100-ppb plumes (from 55 sites)	1000-ppb plumes (from 30 sites)
TCE	55	37	19
PCE	32	20	8
1,1-DCE	29	17	8
cis-1,2-DCE	29	17	7
1,1,1-TCA	23	16	9
Vinyl chloride	20	10	4
1,1-DCA	18	10	2
Chloroform	8	1	0
trans-1,2-DCE	8	0	0
Carbon tetrachloride	7	2	1
1,1,2-TCA	6	0	0
1,2-DCA	6	2	0
Chloroethane	2	1	0
Chloromethane	2	0	0
Methylene chloride	1	1	0
1,1,2,2-TCA	1	0	0
TOTAL	247	134	58

Table 3-2. Summary of frequency distributions of maximum CVOC plume lengths (ft) per site, based on the indicated concentration contour definition.

Quantile	10-ppb-defined plumes	100-ppb-defined plumes	1000-ppb-defined plumes
10^{th}	420	250	90
25^{th}	790	500	230
50^{th}	1600	1100	650
75^{th}	3210	2400	1830
90^{th}	6030	4840	4630

Table 3-3. Fraction of plumes possibly associated with DNAPL for CVOCs represented by more than 10 plumes in the historical case analysis data set.

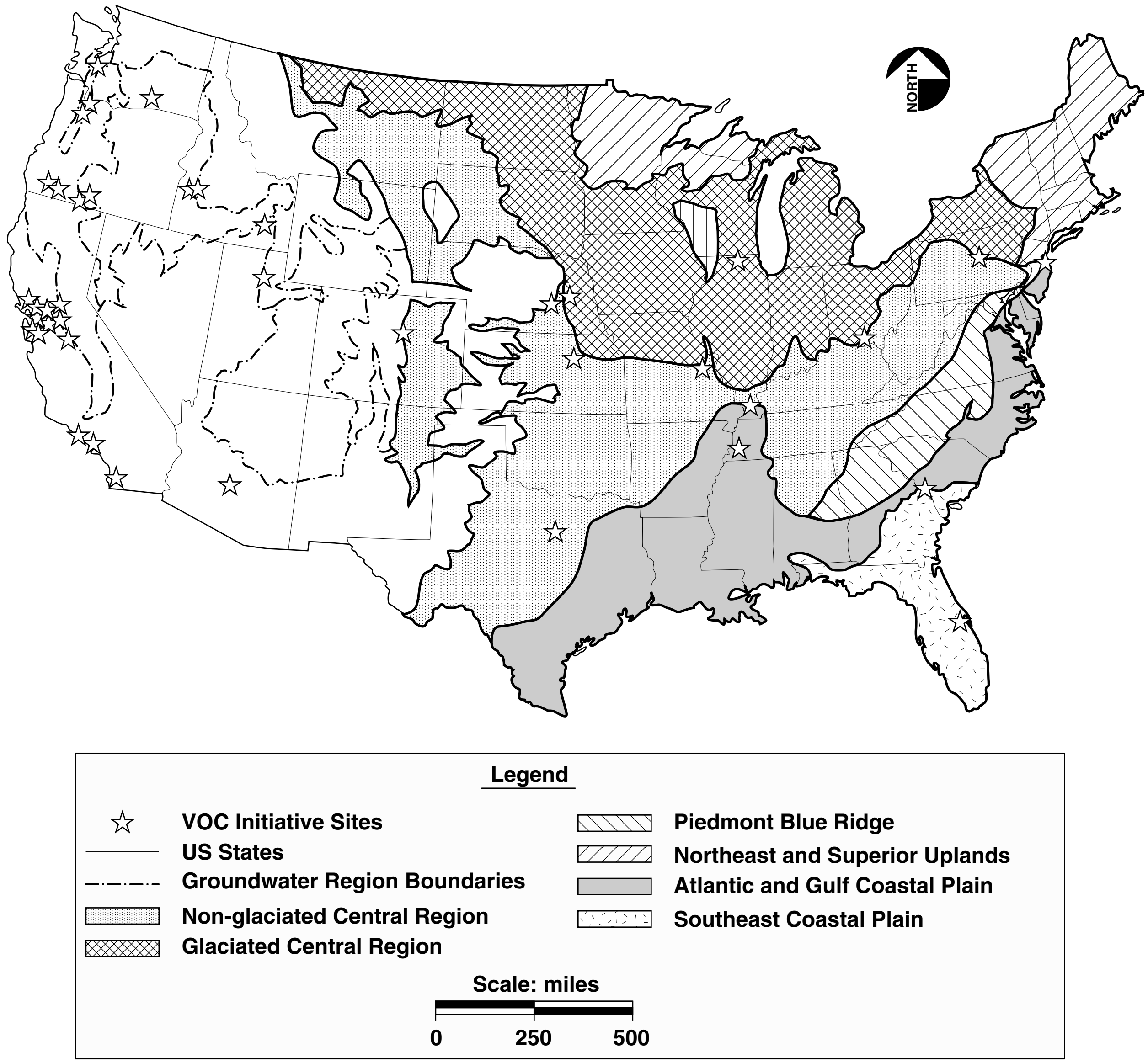
CVOC	Total number 10-ppb-defined plumes	Fraction plumes with conc. > 1% solubility	Fraction plumes with conc. > 10% solubility
TCE	55	36% (20 plumes)	11% (6 plumes)
PCE	32	38% (12 plumes)	13% (4 plumes)
1,1-DCE	29	10% (3 plumes)	0%
cis-1,2-DCE	29	7% (2 plumes)	3% (1 plume)
1,1,1-TCA	23	26% (6 plumes)	4% (1 plume)
Vinyl chloride	20	0%	0%
1,1-DCA	18	0%	0%

Note:

conc. = Concentrations.

Table 3-4. Comparison of TCE parent plume length and reductive dehalogenation sequence daughter product plume length.

Parent/daughter pair	Number of sites with pair	Parent plume is longer	Daughter plume is longer
TCE/*cis*-1,2-DCE	24	18	6
TCE/vinyl chloride	17	13	4
cis-1,2-DCE/vinyl chloride	10	6	4
TOTAL	51	37 (73%)	14 (27%)



States	Number of Sites	States	Number of Sites
California	27	Florida	1
Oregon	10	Illinois	1
Ohio	4	Kansas	1
South Carolina	4	Kentucky	1
Idaho	3	Missouri	1
Washington	3	New Jersey	1
Nebraska	2	Tennessee	1
Pennsylvania	2	Texas	1
Arizona	1	Utah	1

From: S. Belding, 6/29/98

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Figure 3-1. Distribution of VOC study sites in Heath's groundwater regions.

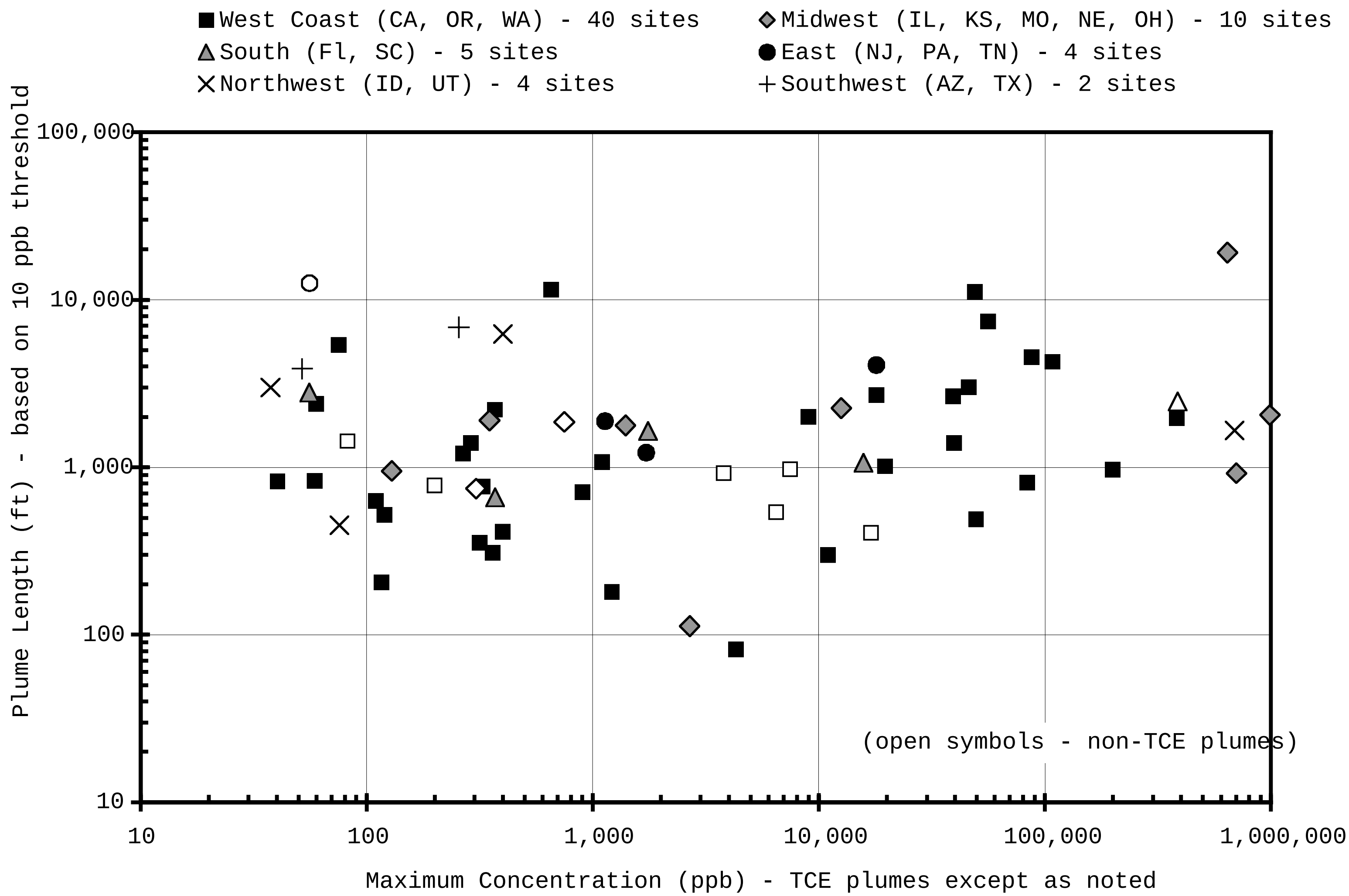

Figure 3-2. Distribution of 10-ppb-defined TCE plumes in terms of plume length and maximum concentration, delineated by region.

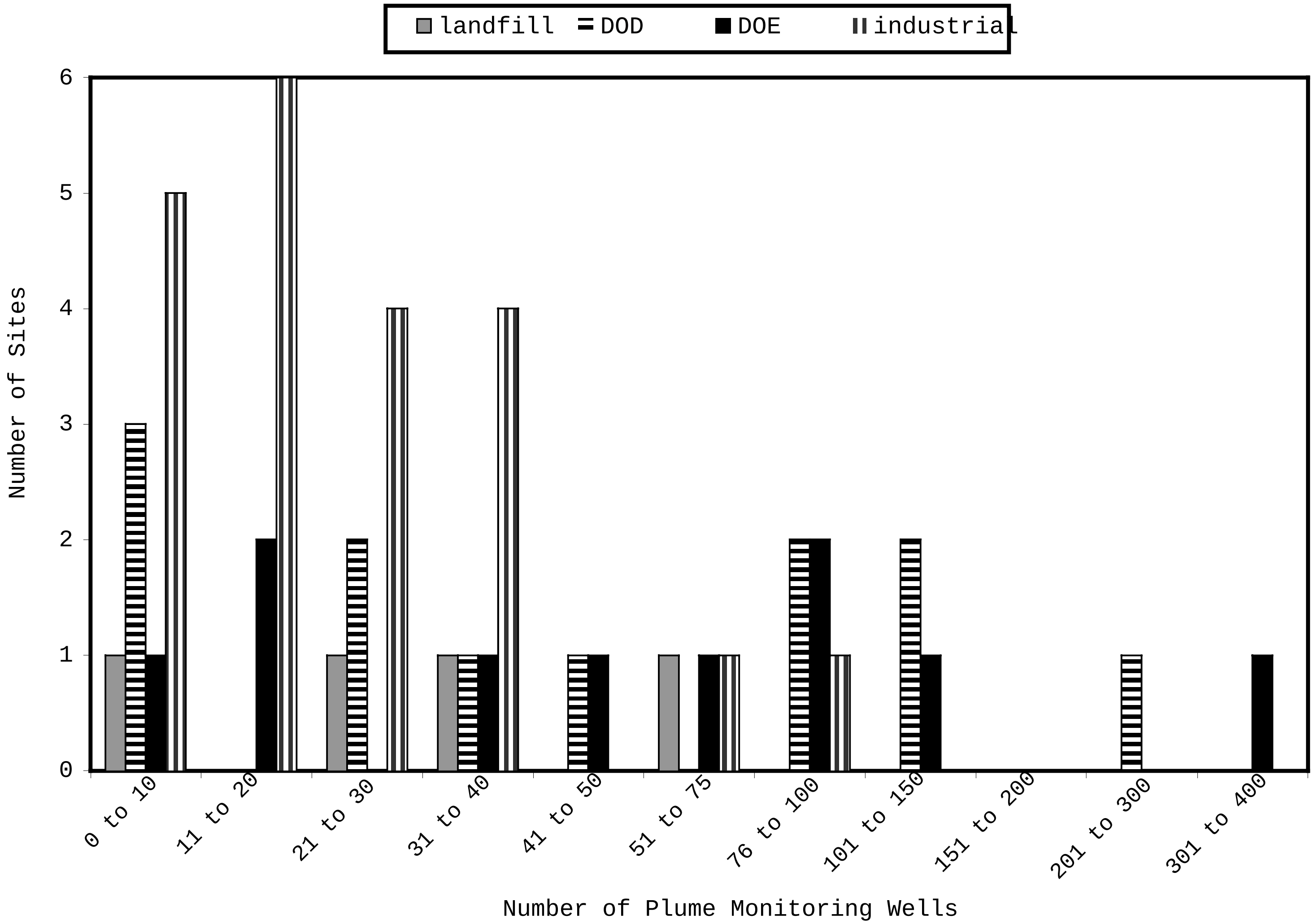

Figure 3-3. Distribution of number of plume monitoring wells by type of site (DOD, DOE, industrial, or landfill).

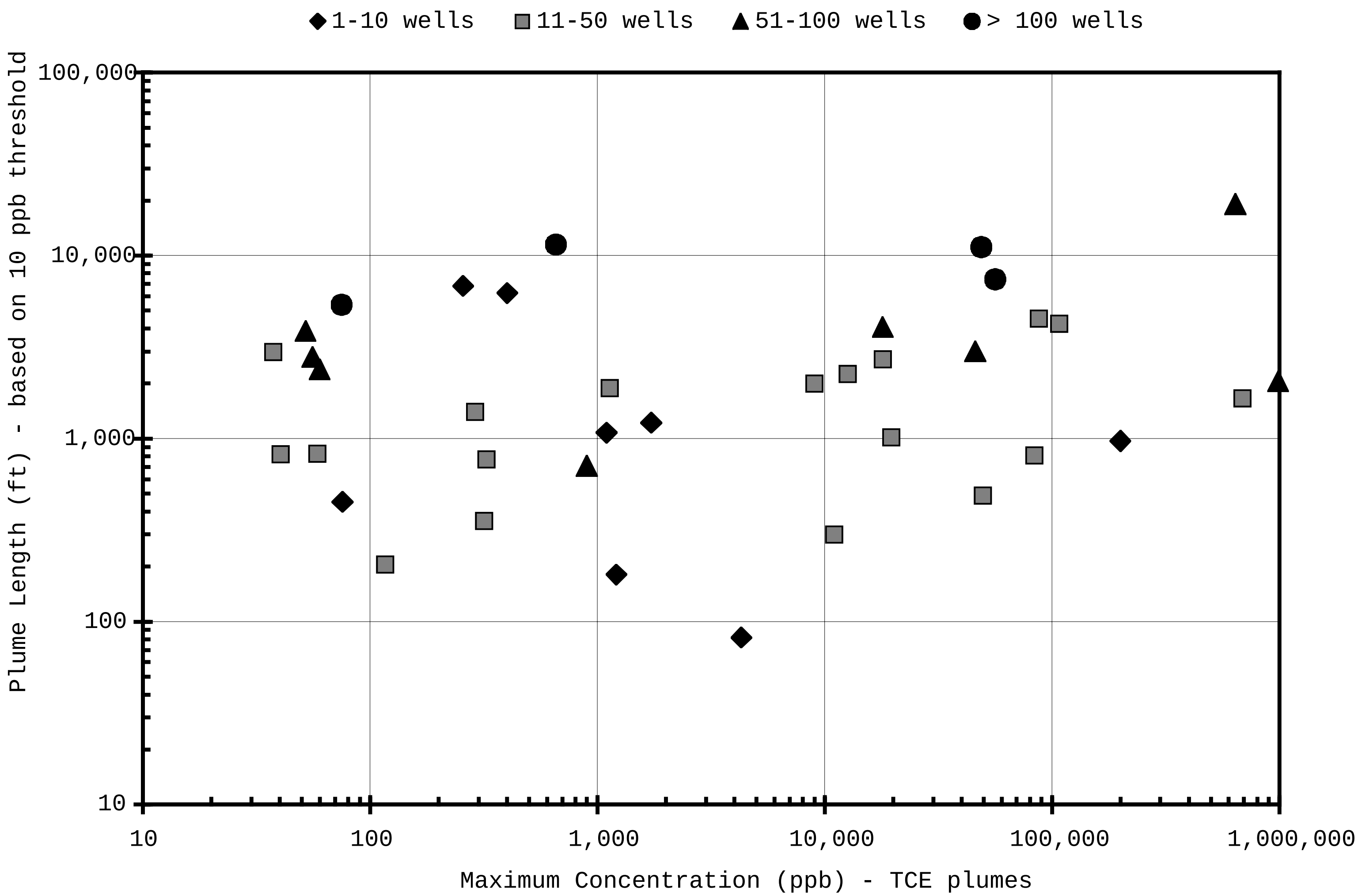

Figure 3-4. Distribution of 10-ppb-defined TCE plumes in terms of plume length and maximum concentration, delineated by number of monitoring wells per site.

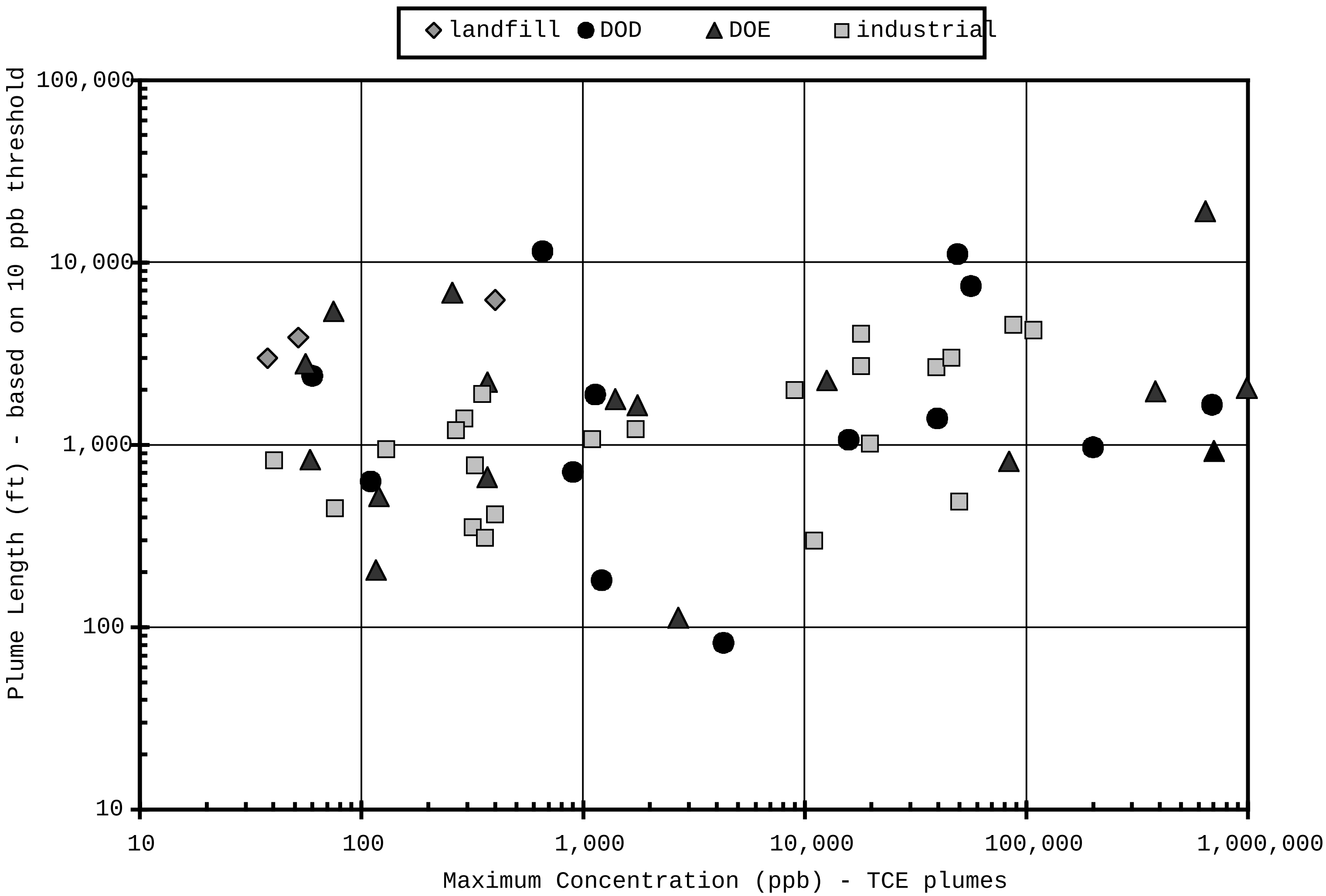

Figure 3-5. Distribution of 10-ppb-defined TCE plumes in terms of plume length and maximum concentration, delineated by type of site.

4. Conclusions

This study provides the first statistical analysis of data from a relatively large population of CVOC plumes and has demonstrated that broad trends in relationships between plume behavior and key site variables can be determined through the statistical analyses of field data from a large number of sites. This finding is important because it demonstrates that:

1. Specific hydrogeologic conditions and contaminant release scenarios at individual sites are not so unique that expected overall trends in the data are completely obscured.
2. Useful average values for site variables such as hydraulic conductivity and groundwater velocity can be quantified in most situations.

This study also shows that statistical methods, such as general linear models and comparison of probability distributions of plume length indices, are useful in quantifying expected relationships between plume length and site variables and CVOC variables within a population of CVOC plumes. In addition, it provides population statistics that may be used to bound the uncertainty inherent in these expected plume behaviors.

The study provides quantitative confirmation that plume behaviors can be grouped and that these groupings are based on expected hydrogeologic processes. An important conclusion of the groupings used in this study is that the presence of *cis*-1,2 DCE without the presence of vinyl chloride may indicate that reductive dehalogenation rates may be insufficient to effectively reduce the extent of CVOC plumes. Another important conclusion is that CVOC transformation rates through dehalogenation have less impact on plume length than source strength and groundwater velocity. Thus, plumes with lower source strength and groundwater velocities may be better candidates for the application of natural attenuation remedies.

4.1. Can Historical Case Data Be Used to Predict CVOC Plume Behavior?

One of the major features of this study is that its analyses and conclusions are based primarily on actual field observations, i.e., data from actual CVOC plume historical cases. At present, there is no evidence that the historical case data can be used predictively outside the range of data reviewed. The strength of the conclusions arising from statistical analyses of the CVOC data are dependent upon data set characteristics, particularly the representativeness and the quality of the data. It must be noted that the plume length distributions, relative plume growth rates, and the types of CVOCs involved are reflective of the 65 sites in the project database, exclusively. There is no way of ascertaining whether or not these distributions present an unbiased sample of the entire population of CVOC plumes across the U.S. without conducting a much larger survey on a vast scale. As more data are added to the CVOC historical data set, representativeness will be enhanced.

On a purely conceptual level, the findings that significant observable relationships between plume length and variables are related to the physics of transport may appear intuitive and obvious. However, it is important to recognize that one of the central issues in conducting historical case analyses of multi-site data is whether or not any common trends may be discerned through the statistical noise created by the specific circumstances associated with individual sites. The significant correlations noted in the data indicate that this is indeed possible. This finding is therefore essential for providing credibility to the other results developed in the study and demonstrating the usefulness of using historical case analysis.

The value of the historical case analysis conclusions for predicting future CVOC plume behavior at a given site must be weighed against known uncertainties in the data and future events. The analysis results represent a retrospective view of a population of CVOC plumes characterized over a relatively short time period. For example, we often do not know over what period of time reductive dechlorination has occurred or may continue to occur at sites, so the long-term or future expectation for reductive dechlorination to occur at a given site is not predictable based on historical data alone.

To use the historical case analysis results to forecast the likelihood of behaviors in future CVOC plume populations requires a link to mechanisms. Since many of the relationships observed in the data are the result of correlation analysis, direct links to cause and effect are not established. The link to mechanisms is established through the use of probabilistic modeling which incorporates the mechanisms of CVOC plume fate and transport. The agreement between probabilistic modeling results and observed plume characteristics enhances the credibility of the data set and the analysis procedures. Furthermore, as new data from existing plumes are added with time, the comparison of new data to the existing historical data will provide direct evidence of the utility of historical case analysis in predicting plume behavior.

4.2. What are Key Uncertainties Associated With Evaluating CVOC Plume Behavior Using Historical Case Data and What Other Types of Data are Needed?

The specific findings, while intuitively reasonable, must be considered preliminary in nature because the modest size of the data set does not statistically capture all of the variability anticipated to exist across CVOC sites with reference to hydrogeology, climate, release scenario, etc. Also, the strength of the conclusions should be tempered by the knowledge that some sites have long plumes and relatively few monitoring wells, which leads to questions about the level of characterization.

Further, it is conceivable that the data used for this historical case analysis may reflect a bias created by the screening checklist criteria. For example, very long plumes may not be included in the data set since pump-and-treat remediation systems may have been installed at such sites early in the site investigation history. Such plumes are also more likely to daylight into surface waters. Small plumes may not be represented sufficiently in the data set; such plumes may not be characterized by a monitoring well network of sufficient size to meet minimum acceptance criterion.

These general limitations are compounded by the incomplete nature of the data in terms of hydrogeologic variables supplied by many of the sites. A more comprehensive data set may shed light on some of the questions that could not be answered completely in this present study or else could not be addressed at all. These questions are discussed further in Section 5.

4.3. How May CVOC Historical Case Analysis Be Used in Cleanup Decision-Making?

The results of this historical case analyses may be used by a site manager to develop initial site conceptual models and help focus characterization resources on data that will be most useful in confirming or denying conceptual model hypotheses. For example, a site manager can measure the length of a CVOC plume to the 10-ppb contour, use maximum groundwater concentrations from a well near the CVOC release area and the mean groundwater velocity to calculate a site-specific plume length index. As explained in Appendix H, the plume length index, calculated by dividing the plume length by the product of the reported maximum concentration and the groundwater velocity, provides a means by which plumes may be compared to one another. Plumes exhibiting strong evidence of reductive dehalogenation tend to be characterized by relatively low plume length indices in comparison to the population of plumes evaluated in this study, as a whole. This information can be used directly to help confirm or refute specific hypotheses developed by site investigators pertaining to the role of reductive dehalogenation. Examples of this approach are presented in Appendix H.

The results of the CVOC historical case analyses also may prove useful to a more general audience. Some examples include:

- The study provides information on the types of data that are not currently being collected that should be collected. For example, the contaminant chemistry was generally found to be the most complete of the types of data reviewed, but data on hydraulic conductivity and organic carbon content of soils and groundwater were less systematically collected and/or reported. Theoretically these parameters should be key to understanding the fate and transport of subsurface contaminants.
- A key practical component to applying a natural attenuation remedial alternative is providing some guarantee that funds will be available for long-term monitoring and implementation of contingency plans if the natural attenuation remedial alternative is shown to have not met expectations. This guarantee may be provided by a performance bond or an insurance policy. The historical case analyses results may provide an actuarial basis for these financial guarantees that is defined in a systematic manner.
- In addition to the scientific findings, an important product of the study was the creation of an electronic database containing hydrogeological, geochemical, and other relevant data for a number of CVOC sites. These data will be made available to other investigators who may conduct future studies.

The precedent set by this study for the utility of statistical analyses of data across a number of sites suggests that the scope of future similar endeavors may include the behavior of plumes under the influence of engineered remediation measures. For example, the effectiveness of pump-and-treat, engineered source removal, and natural attenuation as exclusive remedial measures could be compared to one another across a range of environmental and hydrogeologic settings. Such information could serve a key role in shaping site cleanup decisions by site investigators, stakeholders, and regulatory agencies.

4.4. How Often is a DNAPL Inferred to be Present at Sites Within the CVOC Historical Data Set and What is the Relationship of Inferred DNAPL Presence to the Plume Length at a Given Site?

Reported maximum concentrations for individual CVOCs have been used by other workers as evidence for the presence of an active DNAPL source based on certain established rules-of-thumb, such as 1% or 10% of the solubility limit (Newell and Ross, 1991; and Feenstra and Cherry, 1988, respectively). Based on the rules-of-thumb as indicators of free-phase CVOCs, these observations suggest that the DNAPL may be influencing plume behavior to a certain extent, although not in the case of daughter product species (e.g., *cis*-1,2-DCE, vinyl chloride, possibly 1,1-DCA and 1,1-DCE in some cases). In particular, based on 1% and 10% solubility limit rules-of-thumb, maximum concentrations suggest the presence of DNAPL in a majority of cases where a 1000-ppb TCE plume may be defined.

It must be emphasized that these inferences are based entirely on very general rules-of-thumb that have been established in the contaminant hydrology literature. In reality, there is no direct way of ascertaining whether DNAPLs are present at the sites, given the data provided for this study. However, the relationships between plume length and reported maximum concentration are likely to reflect the overall strength of the source term, which may in turn be influenced by the presence or absence of DNAPL, as well as the capacity for any residual DNAPL to be actively leached into groundwater.

4.5. How Often are Transformation Processes Encountered in CVOC Plumes in the Data Set and What are the Relationships Between the Indications of Transformations and Plume Length?

Based on the presence or absence of *cis*-1,2-DCE and vinyl chloride reductive dehalogenation daughter products, the CVOC sites sampled in this study are divided roughly into equal thirds in terms of no evidence of reductive dehalogenation (no *cis*-1,2-DCE or vinyl chloride plumes), weak evidence of reductive dehalogenation (*cis*-1,2-DCE plumes but no vinyl chloride plumes), and strong evidence of reductive dehalogenation (vinyl chloride plumes present). Analyses of plume length indices (plume lengths adjusted for source strength and groundwater velocity) from the three groups indicate that CVOC plumes exhibit shorter plume lengths at sites where a vinyl chloride plume exists compared to plumes from other sites. The conclusion may be drawn that the presence of a vinyl chloride plume indicates that reductive dehalogenation may be playing a role in reducing the extent of CVOC plumes at approximately one-third of the sites. In contrast, the presence of a *cis*-1,2-DCE plume in the absence of a vinyl chloride plume appears to indicate reductive dehalogenation rates that are insufficient to effectively reduce the extent of CVOC plumes; little evidence exists to suggest that plume lengths and plume growth rates are substantially affected by reductive dehalogenation in these circumstances.

4.6. Do Daughter Product Plumes Behave Differently From Parent CVOC Plumes?

Reductive dehalogenation is a sequential process in which chlorine atoms are removed from a CVOC compound, producing intermediate less-chlorinated daughter products, that may themselves be subject to further transformation(s). Thus, there is an obvious concern that daughter product plumes may develop that might migrate downgradient of the attenuating parent product plume. Indeed, if comparatively high toxicity compounds, such as vinyl chloride, develop substantial downgradient plumes as a result of reductive dehalogenation, an *increased* environmental threat could potentially result.

The analysis of the data in this study indicates that, for the most part, daughter product plumes are contained with, or roughly coincide with, the respective parent product plumes. This finding is supported by several lines of evidence:

- The distributions of logarithms of plume lengths from all sites in the data set among parent and daughter compounds (e.g., PCE, TCE, cis-1,2-DCE, vinyl chloride) do not differ from one another in a statistically significant manner. If parent product species such as PCE or TCE were transformed into daughter products (*cis*-1,2-DCE, vinyl chloride) at rates substantially faster than the subsequent transformations of the daughter products, then *cis*-1,2,-DCE and vinyl chloride plumes would be expected to be much longer, on average, than those of PCE and TCE. This is not the case. One explanation is that *cis*-1,2-DCE and vinyl chloride can continue to undergo reductive dehalogenation to ultimately produce ethene, or may be oxidized to yield carbon dioxide, water, and chloride ions. Recent studies have shown, for example, that vinyl chloride can be oxidized by ferric iron reduction (Bradley and Chapelle, 1996).
- At specific sites with suspected parent-daughter product plume pairs (e.g., TCE/*cis*-1,2-DCE, TCE/vinyl chloride, *cis*-1,2-DCE/vinyl chloride), the parent product plume was observed to be the longer of the two plumes in the majority of cases (37 out of 51, or 73%). Again, if daughter product plumes were systematically recalcitrant in comparison to the parent product plumes, this finding would not be expected. At sites where the daughter product plumes were observed to be longer, the difference in plume lengths was generally on the order of 10%-20% greater than the parent product plume length.
- The offset in locations of observed maximum concentrations of parent and daughter product plumes was, for most plumes, generally on the order of 10%-20% of the parent product plume length, again suggesting a rough coincidence of parent-daughter plumes. However, at approximately one-third of the sites, the maximum concentration offset was greater, on the order of 50% or more of the parent product plume length. A number of explanations could account for this phenomenon, including localized reductive dehalogenation far downgradient of the parent source area, slow reductive transformation rates in comparison to groundwater velocity, or high detection limits of the daughter product in the vicinity of the parent product source area. Nevertheless, even at these sites, the combined parent product-daughter product plume length exceeded that of the parent product alone by greater than 5% in only one-third of the cases. Thus, while the apparent internal morphology of the parent and daughter plumes differed at these sites,

the plume boundaries (as defined by the 10 ppb contour) were roughly coincident in the majority of cases. Refer to Appendix A, Section A-2.1.3 for discussion.

It is important to recognize that these findings all pertain to the *average* behavior of plumes from a sampling large number of sites. At any individual site, a large vinyl chloride plume emanating from a small, attenuating TCE plume could potentially constitute a threat equal to or greater than the original TCE plume if no attenuation had occurred. Such cases must always be carefully investigated on an individual basis. This present study indicates, in a general sense only, that such a scenario is probably less common than not. Potential explanations for this general observation include: (1) subsequent natural attenuation of daughter product plumes (e.g., subsequent biotransformations, dispersion, volatilization), and (2) dominance of other factors, such as groundwater velocity, that may influence plume length.

4.7. What is the Relationship of Fuel Hydrocarbon Co-contamination to CVOC Plume Behavior?

The statistical association between fuel hydrocarbons, elevated bicarbonate alkalinity, and the presence of vinyl chloride plumes provides circumstantial evidence that fuel hydrocarbon co-contamination may be an important factor in the reductive dehalogenation of CVOC plumes in the historical case analysis data set. Elevated manganese concentrations at sites with vinyl chloride plumes is consistent with the presence of an anaerobic environment at these sites. Field evidence suggesting the association between fuel hydrocarbons and reductive dehalogenation has been observed anecdotally by workers at a number of sites (Wiedemeier et al., 1996). The statistical results of the CVOC historical case analysis imply that the phenomenon may be widespread.

It is important to recognize, however, that the West Coast-bias in the site representation in the data set may influence these results. For example, sites from the eastern U.S., characterized by higher precipitation and often a greater preponderance of vegetation, may be characterized by larger quantities of natural organic carbon, which would be available to facilitate reductive dehalogenation. In such instances, the influence of fuel hydrocarbon co-contamination may be less pronounced. A data set that is more uniformly representative of climatic conditions across the U.S. would be required to further illuminate this issue.

The potential association of reductive dehalogenation processes with fuel hydrocarbon co-contamination raises the issue of how long reductive dehalogenation may be sustained at many of these sites. For example, if the source of fuel hydrocarbons is depleted prior to the dissipation of the CVOC plume(s) and a CVOC source still persists, the rate of reductive dehalogenation may be significantly reduced and result in a period of plume growth. This possibility is difficult to address with the data at hand from most of the sites in the CVOC historical case analysis, particularly the lack of historical data over a sufficiently long monitoring period. Thus, while the analysis of site data presented in this study provides a snapshot in time of recent plume behavior, attempts to predict the effect that fuel hydrocarbon presence may have on CVOC plume behavior in the future must be treated as a site-specific issue.

5. Discussion and Recommendations for Future Work

It is clear that variability is a fundamental characteristic of CVOC sites and that conclusions stemming from the current study are general and should not be strictly applicable at any specific site. Although the emphasis in this study is on examining correlations between plume length and hydrogeologic variables, it is apparent that there is enormous variability in both plume length and maximum concentration. For example, plume lengths span two orders of magnitude while maximum concentrations span over four orders of magnitude. Though the numbers of sites in parts of the country other than the West Coast are limited, it appears that variability in plume length and reported maximum concentration occurs in all regions of the country. The addition to the data set of more sites from around the country may show that West Coast sites fully span the range for all CVOC plumes in terms of length, concentration, and site characteristics. However, this cannot be concluded with certainty until the data set is populated with sites from a broader geographic distribution. Indeed, there is no way of ascertaining whether or not the data set presents an unbiased sample of the entire population of CVOC plumes across the U.S. without completing a survey that better represents all the hydrogeographic settings in the U.S.

Continued data collection is recommended because a more comprehensive data set would shed light on some of the questions not answered completely in this present study. These questions include:

- Are there significant differences in plume behavior across different geographic and hydrogeologic regimes (e.g., as specified in Heath, 1984)?
- Is there a dependence of plume behavior on climatic factors such as mean annual rainfall, evapotranspiration rate, or vegetative cover at the site?
- What is the quantification of statistical relationships between site natural organic carbon content and (1) retardation of plume length or normalized plume length and (2) reductive dehalogenation? With regard to reductive dehalogenation in particular, a comparison of the roles of natural organic carbon and anthropogenic carbon sources (e.g., fuel hydrocarbons) would be of significant interest. The finding of the present study that reductive dehalogenation is closely related to the presence of fuel hydrocarbons may be a reflection of a bias in the data set toward the more arid (i.e., low organic carbon content) sites from the western U.S.
- Are there differences in the relationships of plume behavior to site variables, particularly the classes of plumes specifically excluded from this study, e.g., plumes that daylight. As discussed previously, the use of exclusion criteria may systematically under-represent very short and very long plumes in the data set.

In summary, this study sets a precedent for future historical case analysis studies that might include:

1. More detailed analyses of retardation phenomena contingent upon availability of soil TOC data.

2. Geostatistical analyses of plume spatial moments to include dispersion (in three dimensions) as a variable.
3. Development of a significantly expanded data set (i.e., hundreds of sites) that would allow subsets of site classes to be evaluated separately and then be compared to each other.

The ultimate goal of such follow-on studies should be to develop a comprehensive statistical model for plume behavior. This statistical model could provide:

1. Individual site investigators with a plume reference model against which a given plume may be compared and used to identify anomalous behavior.
2. Regulatory agencies with an integrated survey of plume behavior under a variety of conditions.
3. Validation for theoretical models and anecdotal studies of plume behavior within a probabilistic conceptual framework.

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